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(COUPLING WIDTH)

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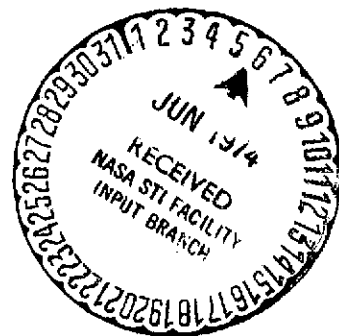
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16. Abstract The untenability of existent theories on the broad- ening of spectral lines in a homogeneous gas is pointed out. An explanation is given for the pronounced broadening which accompanies an increase in the density of the principal gas, according to which this increase is caused by the enhanced decay of the atom resulting from a loss of energy to neigh- boring atoms and by a change in oscillation amplitude, not only with respect to its magnitude but also with respect to sign when atoms pass at short range. The problem is con- sidered in terms of classical and quantum theory. The effect of radiation during collision upon the form and width of lines is studied qualitatively and yields an additional asymmetric broadening effect.			
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BROADENING OF SPECTRAL LINES IN A HOMOGENEOUS GAS*
(COUPLING WIDTH)

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1. Introduction and Summary

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The problem of the broadening of spectral lines in gases due to an increase in the density of the principal gas has long been treated frequently in the literature from both the experimental and the theoretical standpoint. It has been determined experimentally that the broadening associated with an increase in the density of the principal gas is considerably more pronounced than that accompanying the addition of a foreign gas [1-3]¹. This specific broadening of lines due to the interaction of identical atoms has been named coupling width.

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In order to explain coupling width in theoretical terms, a number of experiments were undertaken which must certainly be considered unsatisfactory. The purpose of this article is to fill this gap and to provide a reasonable theory for the excessive broadening of spectral lines which occurs when the density of the gas from which they originate is increased.

The basic idea of most theoretical works on coupling width that have so far appeared is based on the fact that when linear

¹ In the last of these articles, Minkovski, while measuring the natural width of the sodium D line at relatively low pressure, notes a broadening of the line as a function of gas density. See also the summarizing article by V. Weisskopf [4].

* Delivered at the colloquium of the Theoretical Section of the Physics Institute of the Academy of Sciences and of the Scientific Research Institute for Physics at Moscow State University, March 3, 1936.

** Numbers in the margin indicate pagination in the foreign text.

coupling occurs between two equivalent harmonic oscillators, splitting of frequencies takes place, from which it is concluded that the system of equivalent atoms experiencing dipole interaction is already absorbing or emitting in a certain region of the spectrum [5, 6].

Holtzmark, in particular, has calculated the width of this region with the aid of classical theory. He views the gas as a system of N equivalent, immobile, linear harmonic oscillators oriented in parallel which are linked by dipole interaction. Such a system generally possesses N frequencies. Holtzmark has calculated the mean square deviation in the frequency of the system from the frequency of an unperturbed atom and also averages them for all possible positions of the oscillators relative to one another. The quantity $\sqrt{\Delta\omega^2}$ obtained in this manner is equated by Holtzmark with the width of the spectral lines. Frenkel [7] has essentially repeated Holtzmark's studies in terms of quantum /380 theory and has arrived at a similar result. However, Holtzmark's and Frenkel's ideas are not tenable and call for refutation. Weisskopf [8] has subjected them to detailed criticism. We would like to add the following to this criticism: First, in considering the question of the broadening of spectral lines due to interaction of the atoms, we may not replace the gas with a model that consists of immobile, unidimensional, parallel oscillators, since the peculiarities which are essential for the problem to be studied are lost in the process; this can be seen from our further consideration of a model of three-dimensional oscillators in Section 5. Secondly, Holtzmark's theory is not satisfactory within the scope of consideration of the assumed model: it yields a finite broadening of spectral lines even for regularly positioned, linked oscillators, whereas no broadening occurs in this case, but only a shift in the line, as Vlasov has demonstrated exactly [9]². In order for the frequency to appear

² See also Section 2 of our article.

in the spectrum, it is not at all sufficient that it be inherent to the system; rather, in classical terms, it must also be optically active.

For a gas in which the particles are experiencing irregular motion and from time to time can pass one another at short distance, we can assume that only those phenomena are important for the broadening of spectral lines at a limited density which occur as the result of the interaction between two atoms precisely as they approach one another closely. This is the basic idea of Lorentz collision damping, to whose correctness Weisskopf [8, 10] referred for the first time with regard to the case of a homogeneous gas -- in contrast to its consideration as a system of coupled immobile oscillators. The pronounced broadening of spectral lines accompanying compression of the principal gas indicates that it is connected with an interaction between atoms at relatively long distance; thus it is quite natural, in seeking a theoretical explanation of this broadening, to attempt to consider only the dipole forces in the interaction between two equivalent atoms. For this reason, Weisskopf replaces the atoms with identical linear oscillators which interact via the dipole fields and calculates optical collision diameter and, from this, the broadening of the spectral line, which agrees satisfactorily with the experimental data. To be sure, Weisskopf's consideration of collision between the identical atoms is not quite correct. Without sufficient grounds, Weisskopf applies the correct idea of the mechanism of collision damping for non-extinguishing atoms of different types to collisions between identical atoms. We know that the broadening of lines due to collisions occurs not only when the train of waves emitted by the atom departs after collision (extinguishing gas), but also when a change in the phase of oscillation of the excited atom occurs upon collision (nonextinguishing collisions). In order to calculate the phase shift accompanying collision, we must use the

change in frequency $\Delta\omega$ of the emitting atom which results from interaction with foreign atoms, and integrate over collision time; if we set this integral equal to 1, we can evaluate the magnitude of optical collision diameter theoretically. In place of $\Delta\omega$, Weisskopf arbitrarily uses the difference between the frequency of one of the normal oscillations of a system of two dipole-linked identical linear oscillators and the frequency of the isolated atom for collisions between identical atoms. It is clear that this calculation is based on a misunderstanding. $\Delta\omega$ is in essence the change in frequency of the emitting atom, the light from which is analyzed by the Fourier method. Due to degeneration, however, what Weisskopf has used in its place has nothing at all to do with this matter. Lenz [11]³ also commits a similar error /382 following Weisskopf in a later article.

The idea that when two atoms of the same type of which one is excited and the other is not excited collide, the oscillatory phase of the excited atom changes, does not correspond at all to reality. The thermal motion of atoms can be considered slow relative to the intraatomic movement of electrons. If we therefore imagine that an excited atom passes close to a similar atom which is not excited, then the energy of excitation will jump from one atom to the other due to the collapse of the energy level under the influence of the dipole energy of "interaction"; expressed in classical terms, the amplitude of the emitting atom will change. Depending upon the distance at which the atoms pass one another, the excited atom gives up a portion of its energy or all of its energy to the other atom, or a repeated transfer can

³ This error has been repeated time and again until recently, e.g. in the summarizing article by Margenau and Watson [12].

⁴ It must be said that the question of the transfer of energy of excitation between atoms has long been covered in quantum theory by Kallmann and London, but without going into the broadening of spectral lines. See [13] and [14].

take place. It is clear that in the case of ordinary types of excitation, when only an infinitesimal fraction of all atoms are excited, the emitting atom will pass unexcited atoms almost exclusively and will generally lose its energy, and its amplitude will decrease more rapidly than during natural decay. We can describe this phenomenon in part as follows: because the emitting atom moves in the vicinity of unexcited atoms of the same type, the motion of the electron in it experiences an additional "friction." This friction is also one of the causes of the /383 broadening of spectral lines during compression of the principal gas. Aside from this friction effect, which is caused by atoms' passing one another at relatively long distance, i.e. in those cases in which energy can jump in only one direction -- from the particular atom -- still another exists which occurs at shorter ranges (collisions), in which case a more considerable change in the motion of the electron is produced. Here, amplitude can change not only in magnitude but also in direction. Consideration of these short-range collisions causes another component of spectral line broadening which approaches the former in order of magnitude. These two components are additive.

In the work covered by this article, the broadening of spectral lines which accompanies compression of the principal gas was calculated on the basis of the above considerations. For the form of the line, this calculation yields a dispersion-like distribution with a width that is proportional to density and is independent of temperature. The values found theoretically for the magnitude of broadening agree satisfactorily with the empirical data. In our discussion, we shall restrict ourselves to the case of light emission. In Section 3, the atom is replaced with a model consisting of a three-dimensional oscillator whose motion is described by the laws of classical mechanics; even this mode of representation essentially yields correct results, as was also to be expected in the case of the question which is being debated. In Section 4, the quantum theory of broadening is

presented; it yields a result whose difference from the classical result consists of a meaningful refinement. Finally, considerations are presented which make it possible to at least qualitatively cover the effects of the emission which occurs during collision upon the form and width of the line.

2. The Effect of Coupling, Demonstrated with the Example of a Linear Chain

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The content of the preceding paragraphs does not represent anything really new. It is meant to show that the presence of coupling between similar oscillators and thus of frequency splitting is not enough to cause the broadening of a spectral line. The physical reason for this is that the frequencies which occur are the frequencies of the system's normal coordinates. Thus the corresponding oscillations of the individual dipoles assume certain phase relationships. This leads to interference in the emissions of the individual oscillators and, consequently, to the disappearance of several frequencies in the spectrum and, in the case of a regular distribution, for example, to the complete extinction of all except one frequency. In order to demonstrate this, we consider -- for the sake of simplicity -- an infinite linear chain of similar harmonic oscillators which are located at equal intervals from one another and are linked by dipole interaction. If we take the straight line of the chain as the direction of oscillation, we then have

$$-\frac{2e}{|R_k - R_l|^3} x_k \quad \Bigg\}$$

for the force which acts upon the l^{th} oscillator from the k^{th} , where $|R_k - R_l|$ is the distance between the oscillators being considered and ex_k is the electrical moment of the k^{th} oscillator.

The equations of motion are represented by the infinite system

$$\ddot{x}_l + \omega_0^2 x_l = \sum_{k \neq l} a_{kl} x_k; \quad l = 0, \pm 1, \pm 2, \dots, \pm \infty \quad (1)$$

where ω_0 is the cyclic frequency of the isolated oscillator, m is the mass of an electron, and

$$a_{kl} = -\frac{2e^2}{m |R_k - R_l|^3}.$$

We seek the solution to system (1) in the form:

$$x_l = A_l e^{i\omega t}.$$

By substitution, we obtain the system of equations

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$$(\omega_0^2 - \omega^2) A_l = \sum_{k \neq l} a_{kl} A_k \quad (2)$$

for determining A_l . If the oscillators are regularly distributed, system of equations (2) permits exact solution

$$A_l = A_0(u) e^{-i(\omega R_l + \varphi)}$$

If we substitute this into (2), we find that ω and μ are connected by an infinite number of relations of the form

$$\omega_0^2 - \omega^2 = \sum_{k \neq l} a_{kl} e^{i\mu(R_k - R_l)}; \quad l = 0, \pm 1, \pm 2, \dots, \pm \infty$$

Due to the regularity of distribution of the oscillators, however, all become identical, since the sum on the right side of these relations does not depend upon the number l and, if we

collect terms with the same modulus $|k - \ell| = s$ by pairs in the sum, yields

$$\omega_0^2 - \omega^2 = 2 \sum_{s=1}^{\infty} a_s \cos \mu s d \quad (3)$$

where d indicates the distance between neighboring oscillators. The solution to the infinite system of equations (1) will thus be represented in the form of traveling waves from oscillator elongations. Relation (3) yields the dispersion law for these waves. We see that the system under consideration possesses an unlimited multiplicity of frequencies, which are determined from equation (3) for each μ ; $|\mu|$ can apparently range through all values from zero to a certain maximum which depends upon d .

Let us consider the radiation from the chain and look at the radiation which corresponds to the dipole wave of a particular wave number. In this case, the electric moment of the k^{th} oscillator will have the value

$$P_k(\mu) = e A_0(\mu) e^{i(\omega t - \mu k d)}$$

If we calculate the intensity of radiation at a relatively large /386 distance from the chain (Fraunhofer's case!) in the direction which forms the angle θ with a perpendicular to it, then the phase of radiation from the k^{th} oscillator will be at a distance from phase $k = 0$ which -- if we disregard phase shift $\mu k d$ -- is increased by the amount

$$\omega \frac{k d \sin \theta}{c} = \mu k d \sin \theta$$

where $x = \omega/c$, and c is the velocity of light. Light excitation S , which is being sought, can be represented as

$$S = \text{const.} \sum_{k=-\infty}^{+\infty} e^{i(\omega t - kd(\mu + x \sin \theta))}.$$

Since $\lambda > d$ for visible light, we can convert the sum into the integral

$$S = \text{const.} e^{i\omega t} \int_{-\infty}^{+\infty} e^{-iz(\mu + x \sin \theta)} dz = \text{const.} e^{i\omega t} \delta(\mu + x \sin \theta)$$

where δ represents the Dirac δ function, which differs from zero only at the point $\mu + x \sin \theta = 0$. We thus find that, out of the "continuum" of possible frequencies for the chain in the optical spectrum, only one occurs, for which

$$\mu + x \sin \theta = 0.$$

We find the magnitude of this "optically active" frequency by substituting the value of μ from (4) into relation (3). In the case of observation perpendicular to the chain, $\theta = 0$, the condition for optical activity will simply be

$$\mu = 0$$

and, for the optically active frequency,

$$\omega_0^2 - \omega^2 = \sum_{k \neq l} a_{kl} \quad (5)$$

which coincides with formula (9) in the article cited [9]. Since $\lambda > d$ and a_s decreases rapidly as s increases, the frequencies emitted at other angles will also differ only slightly from that shown in formula (5).

Thus the presence of a dipole link between the regularly positioned oscillators does not produce a broadening of the lines, but only their displacement, the magnitude of which is determined by formula (5)⁵. As the calculation which we made with the aid of perturbation theory shows, even just small fluctuations in the distribution of atoms in the chain, which occur as the result of thermal motion, produce no broadening of the line, as a first approximation. Consideration of the three-dimensional case likewise presents nothing that is essentially new⁶. For an explanation of line broadening in a gas, it is therefore more correct not to proceed from the consideration of a system of immobile atoms, but rather of atoms which are experiencing random motion, and to take only those phenomena into consideration which occur as they approach one another.

3. Classical Approach

We now assume the task of calculating spectral line width for radiation emitted by a homogeneous gas. This radiation is studied by first passing it, for example, through a Nicol prism whose plane of oscillation lies parallel to the z-axis. We neglect natural decay and the Doppler effect here, and concentrate on broadening as a function of gas density.

Let us assume that the line being considered corresponds to a transition of the atom to the ground state. We shall conceive of the atom itself in the form of the classical model of a three-dimensional harmonic oscillator of cyclic frequency ω_0 . Let us

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⁵ In the case of absorption lines, the shift indicated by formula (5) corresponds to what is obtained from the Lorentz-Lorenz formula for the complex refractive index. The possibility of finding it experimentally has been covered in detail by Weisskopf [4].

⁶ Cf. [15].

the vicinity of the remaining atoms, and we study its radiation. In addition, we shall neglect gas-kinetics collisions, i.e. those collisions which appreciably alter the motion of the atom, since they are relatively rare. We shall imagine the atom to move linearly and uniformly at velocity v . We shall first study the effect which the movement of the atom past another, unexcited atom has upon electronic oscillation. Let the unexcited atom be located at the origin of the system of coordinate axes x, y, z , and let x_1, y_1, z_1 be the coordinates of its electron, and x_2, y_2, z_2 be the electron coordinates of the excited atom in the system, which moves with it and parallel to the first system. If the distance R between the atoms is considerable relative to their size, we can then expand the potential energy due to forces of Coulombic interaction with respect to powers of $x_1/R, y_1/R, \dots, z_2/R$ and restrict ourselves to the first nonoscillating terms; this yields the familiar potential energy expression for dipole interaction, which reads as follows in our coordinate system:

$$V = \frac{e^2}{R^3} [x_1 x_2 (1 - 3 \cos^2 \alpha) + y_1 y_2 (1 - 3 \cos^2 \beta) + z_1 z_2 (1 - 3 \cos^2 \gamma) - 3(x_1 y_2 \cos \alpha \cos \beta + x_1 z_2 \cos \alpha \cos \gamma + y_1 x_2 \cos \beta \cos \alpha + y_1 z_2 \cos \beta \cos \gamma + z_1 x_2 \cos \gamma \cos \alpha + z_1 y_2 \cos \gamma \cos \beta)]. \quad (6)$$

Here, e is the charge of an electron and α, β, γ are the angles between radius vector R and the coordinate axes.

The equations of motion for the electrons of the first and second atoms will assume the following form, taking interaction (6) into consideration:

$$\left. \begin{aligned} x_1 + \omega_0^2 x_1 + \lambda [(1 - 3 \cos^2 \alpha) x_2 - 3 \cos \alpha \cos \beta y_2 - 3 \cos \alpha \cos \gamma z_2] &= 0 \\ y_1 + \omega_0^2 y_1 + \lambda [(1 - 3 \cos^2 \beta) y_2 - 3 \cos \beta \cos \alpha x_2 - 3 \cos \beta \cos \gamma z_2] &= 0 \\ z_1 + \omega_0^2 z_1 + \lambda [(1 - 3 \cos^2 \gamma) z_2 - 3 \cos \gamma \cos \alpha x_2 - 3 \cos \gamma \cos \beta y_2] &= 0 \\ x_2 + \omega_0^2 x_2 + \lambda [(1 - 3 \cos^2 \alpha) x_1 - 3 \cos \alpha \cos \beta y_1 - 3 \cos \alpha \cos \gamma z_1] &= 0 \\ y_2 + \omega_0^2 y_2 + \lambda [(1 - 3 \cos^2 \beta) y_1 - 3 \cos \beta \cos \alpha x_1 - 3 \cos \beta \cos \gamma z_1] &= 0 \\ z_2 + \omega_0^2 z_2 + \lambda [(1 - 3 \cos^2 \gamma) z_1 - 3 \cos \gamma \cos \alpha x_1 - 3 \cos \gamma \cos \beta y_1] &= 0 \end{aligned} \right\} \quad (7)$$

where we use the abbreviation

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$$\lambda = \frac{e^2}{m R^3}$$

and m is the mass of an electron. In these equations, α, β, γ and λ are given time functions. Since the velocity due to the thermal motion of the atoms is low compared to the intraatomic motion of electrons, we can assume that these functions change only slowly with respect to the inherent frequency of the change in coordinates. To be sure, the change in these parameters due to degeneracy of the system is not adiabatic in Ehrenfest's sense, so we cannot apply the methods of solution which are usual in these cases; we therefore employ the method of successive approximations to solve system of equations (7). The terms which express coupling in this system, i.e. those terms which contain λ , are small; thus we can transfer them to the right side and substitute the known approximations for the sought functions into them. For the 0th approximation we use⁷

$$x_1^{(0)} = y_1^{(0)} = z_1^{(0)} = x_2^{(0)} = y_2^{(0)} = 0$$

and

$$z_2^{(0)} = A \cos \omega_0 t.$$

If we substitute these values into the terms containing λ in equations (7) and then solve them, we can obtain the functions

⁷ For the sake of simplicity, we assume an excitation mechanism here in which the linear mode of oscillation of the electron is excited.

being sought as a first approximation⁸.

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$$\left. \begin{aligned} x_1^{(1)} &= \frac{3A}{2\omega_0} \int_0^t \lambda \cos \alpha \cos \gamma dt \cdot \sin \omega_0 t \\ y_1^{(1)} &= \frac{3A}{2\omega_0} \int_0^t \lambda \cos \beta \cos \gamma dt \cdot \sin \omega_0 t \\ z_1^{(1)} &= -\frac{A}{2\omega_0} \int_0^t \lambda (1 - 3 \cos^2 \gamma) dt \cdot \sin \omega_0 t \\ x_2^{(1)} &= y_2^{(1)} = 0; \quad z_2^{(1)} = A \cos \omega_0 t \end{aligned} \right\} \quad (8)$$

⁸ Solutions (8) are a generalization of the resonance formula for the case of a force of slowly varying amplitude. They can easily be obtained on the basis of the following considerations: let η_1 satisfy the oscillation equation with the right member

$$\ddot{\eta} + \omega_0^2 \eta = N(t).$$

Given starting conditions $\dot{\eta}(0) = \eta(0) = 0$, then its solutions (for example, see [16]) will be

$$\eta(t) = \frac{1}{\omega_0} \int_0^t N(\tau) \sin \omega_0(t - \tau) d\tau; \quad (A)$$

when $N(t) = \alpha(t) \cos \omega_0 t$ and $\alpha(t)$ varies little during one period, we can rewrite (A) approximately as follows:

$$\begin{aligned} \eta(t) &= \frac{1}{2\omega_0} \left\{ \sin \omega_0 t \int_0^t \alpha(\tau) (1 + \cos 2\omega_0 \tau) d\tau - \cos \omega_0 t \int_0^t \alpha(\tau) \sin 2\omega_0 \tau d\tau \right\} = \\ &= \frac{1}{2\omega_0} \sum_k \left\{ \sin \omega_0 t \alpha(\tau_k) \left[\int_{kT}^{(k+1)T} d\tau + \int_{kT}^{(k+1)T} \cos 2\omega_0 \tau d\tau \right] - \right. \\ &\quad \left. - \cos \omega_0 t \alpha(\tau_k) \int_{kT}^{(k+1)T} \sin 2\omega_0 \tau d\tau \right\}; \end{aligned}$$

if we set $T = 2\pi/\omega_0$, for example, and assume that $t \geq T$ -- neglecting the small terms -- we finally arrive at the formula

$$\eta(t) = \frac{1}{2\omega_0} \sin \omega_0 t \sum_k \alpha(\tau_k) \Delta \tau_k = \frac{1}{2\omega_0} \int_0^t \alpha(\tau) d\tau \cdot \sin \omega_0 t.$$

These solutions show that oscillations of the unexcited atoms are induced in the first approximation.

Let us calculate the state of motion which the electron experiences initially in the unexcited atom after the emitting atom has passed it. We shall at first limit ourselves to passing at long ranges. What this refers to will become clear below. The calculation of higher-order approximations for the solutions /391 to equations (7) shows that only in the case of oscillation amplitudes do changes result that occur in the form of rapidly decreasing series; thus the amplitudes x_1, y_1, z_1 do not change in the second approximation, for example, and the changes which occur for them will be only third-order, fifth-order, etc. We therefore use the solutions in the first approximation from formula (8) for passing at long ranges. We let $\alpha_1, \beta_1, \gamma_1$ be the angles between the direction of the excited atom's path and the coordinate axes, ρ the perpendicular which is dropped from the unexcited atom to the direction of motion, and $\alpha_2, \beta_2, \gamma_2$ the angles which it forms with the coordinate axes. In order to determine the amplitude of oscillation of the electron in the initially unexcited atom, we assume that the atoms interact during the course of time τ , interaction beginning at time $t = 0$, when the emitting atom is located at a distance of $-\tau v/2$ from the base of the perpendicular ρ . From formula (8), amplitude, e.g. $x_1^{(1)}$ after a pass will appear as follows:

$$X_1^{(1)} = \frac{3A}{2\omega_0} \int_0^\tau i \cos \alpha \cos \gamma d\tau' \quad (9)$$

On the basis of elementary analytical geometry considerations, we have

$$\left. \begin{aligned} \cos \alpha &= \frac{\rho \cos \alpha_2 + v(t - \frac{1}{2}\tau) \cos \alpha_1}{R} \\ \cos \beta &= \frac{\rho \cos \beta_2 + v(t - \frac{1}{2}\tau) \cos \beta_1}{R} \\ \cos \gamma &= \frac{\rho \cos \gamma_2 + v(t - \frac{1}{2}\tau) \cos \gamma_1}{R} \\ R^2 &= \rho^2 + v^2(t - \frac{1}{2}\tau)^2. \end{aligned} \right\} \quad (10)$$

If we substitute these values into (9) and introduce the new variable of integration $t' = t - (1/2)\tau$, we then obtain

$$X_1^{(0)} = \frac{3.4}{2\omega_0 m} \int_{-\infty}^{+\infty} \frac{(\rho \cos \alpha_2 + vt' \cos \alpha_1)(\rho \cos \gamma_2 + vt' \cos \gamma_1)}{V(\rho^2 + v^2 t'^2)^{3/2}} dt'. \quad (11)$$

Analogous expressions are also obtained for $Y_1^{(1)}$ and for $Z_1^{(1)}$ from 392 (8). In these expressions, we can set τ equal to ∞ . The resultant integrals can then be evaluated analytically, and we ultimately obtain the following formula for the oscillation amplitudes of the electron in the initially unexcited atom after an excited atom has passed it at range ρ :

$$\left. \begin{aligned} X_1^{(0)} &= \frac{e^2}{m\omega_0} \cdot \frac{A}{\rho^2 v} (2 \cos \alpha_2 \cos \gamma_2 + \cos \alpha_1 \cos \gamma_1) \\ Y_1^{(0)} &= \frac{e^2}{m\omega_0} \cdot \frac{A}{\rho^2 v} (2 \cos \beta_2 \cos \gamma_2 + \cos \beta_1 \cos \gamma_1) \\ Z_1^{(0)} &= \frac{e^2}{m\omega_0} \cdot \frac{A}{\rho^2 v} (2 \cos^2 \gamma_2 + \cos^2 \gamma_1 - 1) \end{aligned} \right\} \quad (12)$$

The magnitude of transferred energy ε can easily be determined from these equations; for this purpose, we must square the amplitudes and add them after first multiplying them by $m\omega_0^2/2$. If we do this and apply the condition that v and ρ be perpendicular, we obtain

$$\varepsilon = \frac{e^4}{m^2 \omega_0^2 \rho^4 v^2} \sin^2 \gamma_1 \cdot E, \quad (13)$$

where $E = m\omega_0^2 A^2 / 2$ represents the oscillatory energy of the electron in the passing excited atom. It is interesting to note that ϵ is a function of γ_1 , i.e. of the angle which the direction of the relative velocity of the atoms forms with the direction of polarization of the light emitted by the atom.

Formula (12) for the amplitudes can be used for ranges down to those at which the entire energy can jump to the unexcited atom. The equation

$$\epsilon = E \quad (11)$$

gives us the minimum value ρ_0 down to which we can still describe path range as long. From (13) and (14), we have

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$$\frac{1}{\rho_0^2 v} = \frac{m\omega_0}{e^2}, \quad (15)$$

where we have replaced $\sin \gamma_1$ with its maximum value⁹.

Thus the emitting atom will impart energy ϵ as given by formula (13) to the unexcited atom at a range which is not very short. This energy is transferred essentially during that time in which the excited atom is located close to the base ρ of the perpendicular dropped from the unexcited atom to its trajectory. We can therefore take the following approach in order to

⁹ A direct evaluation of the higher-order approximations in the solutions to equations (7) shows that even for passes at range ρ_0 , the next change in amplitudes x_1, y_1, z_1 is no more than 20% of the first approximation values from equations (8). In place of $\sin \gamma_1$ we have taken its maximum value, since we can use the first approximations only if they remain small for all values of t , not just for $t = \infty$; our formulas (12) satisfy this. For $\gamma_1 = 0$, for example, our formulas (12) yield values of zero down to $\rho = 0$ for the first approximations, though these approximations are not monotonic functions of time in this case, and the value ρ_0 from the maximum for ϵ yields a value on the same order as formula (15).

calculate the entire energy loss that occurs from a long passing range as the emitting atom moves through the homogeneous gas over a distance $\Delta s = vdt$: We sum the energies obtained from formula (13) for all of the atoms which are located farther than ρ_0 in the layer Δs thick standing perpendicular to the trajectory; if N is the number of atoms per unit volume, we then obtain the following for energy loss¹⁰:

$$dE = -2\pi N \Delta s \int_{\rho_0}^{\infty} \epsilon_r d\rho = -\pi N \Delta s \frac{e^4}{m^2 \omega_0^2} \sin^2 \gamma_1 \frac{1}{\rho_0^2} E. \quad (16)$$

or ultimately, from (15):

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$$dE = -\pi N \frac{e^2}{m \omega_0} \sin^2 \gamma_1 E dt.$$

If we average this expression over γ_1 ¹¹ and integrate, we obtain

$$E = E_0 e^{-\nu' t_0}. \quad (17)$$

where E_0 is the initial energy of the excited atom, and

$$\nu' = \frac{2\pi}{3} \cdot \frac{Ne^2}{m \omega_0}. \quad (18)$$

¹⁰ Strictly speaking, all of our calculations are correct as long as the distances being considered are short compared to the length of a light wave. It can easily be seen that this is satisfied for the cases which are of interest to us, since the values ρ_0 obtained from formula (15) are on the order of 10^{-7} cm. The infinite limits of integration in integrals (11) and (16) do not come under consideration, since the integrand decreases sufficiently rapidly.

¹¹ See Supplement I.

It can be seen from equation (17) that even in the absence of collisions, a decay of electronic oscillations occurs in the emitting atom. In order to determine the width of the spectral line caused by this decay, we must halve (18); we thereby obtain the following for the sought half-value width δ_r' (the distance from the maximum to the value at which intensity drops to one-half), expressed in the scale of cyclic frequencies:

$$\delta_r' = \frac{\pi}{3} \frac{e^2}{m\omega_0} \cdot N. \quad (19)$$

Stated exactly, we obtain the width of the Fourier expansion for oscillations of the oscillator under consideration in this manner; for line width, on the other hand, we need the expansion for radiation which in our case is obtained from the radiation of the initially excited atom and the radiations from those atoms which have received energy from it, since the damping mechanism taken into consideration does not provide for conversion of the light into any other form of energy. To be sure, we cannot consider this repeatedly excited radiation to interfere with the original radiation; this can be seen immediately for its x- and y-components; as far as the z-component is concerned, it too will not be coherent, due to motion of the atoms, since as the discussed decay begins to become appreciable at low gas density, the atom can cover a distance, prior to finally emitting its light, that amounts to a multiple of the light's wavelength. We can thus assume that the width of the spectral lines coincides with the width of the Fourier analysis for oscillations of the oscillator which was initially excited. The transferred energy must, in the case of absorption, be the cause of additional light dispersion, which will probably be operant only in the region near ω_0 (selective scattering). /395

In order to arrive at a correct result, we must apply a correction to the classical calculation: we must multiply the

quantity e^2/m by oscillator strength f ; this is obtained directly from quantum theory (see next section).

Thus the width obtained, $\delta_r = f\delta_r^t$, which results only from long path ranges, already has the correct value and corresponds in order of magnitude to experimental observations. In addition, however, we also have short pass ranges, i.e. those at which the distance between atoms is less than ρ_0 , which is determined by formula (15); we wish to call these collisions. The effect of collisions on the width of the spectral lines cannot be determined just by the energy loss, since the oscillatory amplitude of the electron can change not only in magnitude during them, but also in sign, as can be seen from the calculation of the next higher-order approximations for solutions to system of equations (7). The change in amplitude is a function of the distance at which the atom passes and, since the value of this distance within ρ_0 is random, we can assume that positive and negative values of amplitude which do not exceed their value prior to collision in absolute magnitude are equally probable after collision. In other words, we expect a discontinuous change in amplitude at the instant of collision such that its mean is equal to zero. Such a concept for the collision mechanism leads to results which are analogous to the ordinary Lorentz¹² theory of collision damping, i.e. it yields the same line width and form. Our approach allows us to theoretically determine the principal parameter in Lorentz's theory -- optical collision diameter; in our case, optical collision diameter will be the quantity ρ_0 given in formula (15). For the line width due to collisions we obtain

$$\gamma_k = \pi \omega_0^2 N v = \pi \frac{e^2}{m \omega_0} N. \quad (20)$$

¹² See Supplement II.

By combining (19) and (20) and multiplying by f , we obtain the final expression for the width of the spectral line in a homogeneous gas:

$$\delta = f(\delta_r' + \delta_s') = \frac{4\pi}{3} f \frac{e^2}{m\omega_0} N. \quad (21)$$

This formula differs only by the coefficient $8/3$ from the expression which Weisskopf [4] has already compared with experiment. Weisskopf found here that agreement with experiment is satisfactory. Our formula gives a value which is approximately three times as large for line width than does Weisskopf's formula, and this is a correction in the right direction -- to say nothing of the fact that the conclusion indicated by Weisskopf's formula is untenable -- since the values indicated by Weisskopf are in all cases smaller than observed experimentally. To be sure, we can still not use our formula to explain the pronounced broadening of the mercury line observed by Ortmann and Pringsheim [2]; according to the measurements by these authors, the width observed experimentally exceeds the theoretical value given in formula (21) by a factor of approximately five. The ideas developed later (in Section 5) show that we must consider expression (21) to be the lower limit for the value of spectral line width in a homogeneous gas. We can therefore assume that Ortmann and Pringsheim's results do not contradict the theory which has been developed. It should also be noted that the dispersive distribution of line intensity occurs, when the friction effect is taken into consideration, in the case in which oscillation amplitude falls off strictly exponentially. In reality, however, the exponential decrease in amplitude is somewhat deformed, as can be seen from the physical cause of friction; we can probably relate this to the slower regression in intensity observed experimentally by Minkowski [3] than in the case of the dispersion formula, since these deformations must have a more pronounced

effect on the intensity of those frequencies which are far from ω_0 (on the "wings" of the line). It is precisely at this point that Minkovski also made his measurements. To be sure, it is difficult to evaluate the value given on the above-mentioned grounds, even in order of magnitude, in order to be able to state with certainty that the experimental observations can be explained.

We now go to a quantum theory consideration of the problem. It provides a result which is analogous to the classical theory which has been discussed and thus serves as confirmation of the correctness of the results obtained by classical means.

4. Quantum Theory Approach

We know that the natural width of spectral lines is caused, in quantum theory, by the uncertainty of energy terms which result from the finiteness of the lives of excited states. In the case of an isolated atom, the life of the excited state is determined only by interaction with the radiation field. In our case, however, we have not only the atom's interaction with the field but also an interaction with other identical atoms, which causes a /398 shortening of the life of the excited state and thus produces an additional uncertainty in the terms. At a sufficient gas density, uncertainty in energy terms due to the second cause will predominate. Thus we can neglect the broadening of energy levels due to the loss of energy to the radiation field, and we need consider only the transfer of energy to surrounding atoms. Accordingly, we can approach the solution of this task as follows: Without considering decay due to radiation, we shall have to determine the change in the probability amplitude of the excited state with time due to the presence of a link with other atoms. Due to the specific degeneracy of the problem (equivalent atoms), the probability amplitude of the excited state changes -- even with limited coupling (dipole energy of interaction, long pass ranges) -- to a much greater degree than due to the presence of a coupling

with the radiation field. If we substitute the value found in this manner for the probability amplitude of the excited state into the equations of Dirac's radiation theory, which yield a change in the probability amplitudes of both the atomic states and the radiation field, we can determine the latter. The distribution of probability amplitudes over the frequencies of oscillators in the radiation field will also yield the width of the spectral line.

Let us determine the change in the probability amplitude of the excited state for the case in which the emitting atom passes close to the unexcited atom. We shall describe the motion of the atoms themselves classically and restrict ourselves to a consideration of long pass ranges only; their exact determination, in analogy to the classical, will also be given below. For the energy of interaction we use the dipole energy of interaction given in formula (6) for this reason. As the result of atomic motion, the energy of interaction will not be constant, and its dependence /399 upon time will be determined from formula (10). In further discussion, we shall limit ourselves to the case of atoms with a spherically symmetrical field. For the additional states, we assume an s-state for the first (unexcited) atom and designate the amplitude of its wave function $\psi_{n00}(1)$, where the subscripts are the quantum numbers n, l, m . For the second, emitting atom, we assume a wave function of the form

$$a\psi_{m10}(2) + c\psi_{n00}(2), \quad (22)$$

corresponding to the polarization of emitted light along the z-axis.

Since the possibility exists of an exchange of energy between the individual atoms, the system under consideration possesses six-fold degeneracy, due to the three-dimensional degeneracy of the excited state of two identical atoms. As a result of the

slowness of the atoms' thermal motion, the transitions will essentially take place between the isoenergetic states. We therefore seek the wave function for an arbitrary time during passing in the form of a linear combination of the functions:

$$\Psi(1, 2, t) = \left\{ a_1(t) \psi_{n00}(1) \psi_{m10}(2) + a_2(t) \psi_{n00}(1) \psi_{m11}(2) + \right. \\ \left. + a_3(t) \psi_{n00}(1) \psi_{m1-1}(2) + b_1(t) \psi_{m10}(1) \psi_{n00}(2) + \right. \\ \left. + b_2(t) \psi_{m11}(1) \psi_{n00}(2) + b_3(t) \psi_{m1-1}(1) \psi_{n00}(2) \right\} e^{i \frac{E_n + E_m}{\hbar} t} + \\ + c_1(t) \psi_{n00}(1) \psi_{n00}(2) e^{i \frac{2E_n}{\hbar} t}. \quad (23)^{13}$$

If we substitute (23) into the wave equation

$$\left[H(1) + H(2) + V(1, 2, t) - i\hbar \frac{\partial}{\partial t} \right] \Psi(1, 2, t) = 0$$

and take into consideration that the mean values of the coordinates of the electrons are equal to zero in the unperturbed state, we then obtain the system of equations for determining the coefficients as functions of time in the conventional manner: /400

$$\left. \begin{aligned} i\hbar \frac{db_1}{dt} &= V_{n00; m10}^{m10; n00} a_1 + V_{n00; m11}^{m10; n00} a_2 + V_{n00; m1-1}^{m10; n00} a_3 \\ i\hbar \frac{db_2}{dt} &= V_{n00; m10}^{m11; n00} a_1 + V_{n00; m11}^{m11; n00} a_2 + V_{n00; m1-1}^{m11; n00} a_3 \\ i\hbar \frac{db_3}{dt} &= V_{n00; m10}^{m1-1; n00} a_1 + V_{n00; m11}^{m1-1; n00} a_2 + V_{n00; m1-1}^{m1-1; n00} a_3 \\ i\hbar \frac{da_1}{dt} &= V_{m10; n00}^{n00; m10} b_1 + V_{m11; n00}^{n00; m10} b_2 + V_{m1-1; n00}^{n00; m10} b_3 \\ i\hbar \frac{da_2}{dt} &= V_{m10; n00}^{n00; m11} b_1 + V_{m11; n00}^{n00; m11} b_2 + V_{m1-1; n00}^{n00; m11} b_3 \\ i\hbar \frac{da_3}{dt} &= V_{m10; n00}^{n00; m1-1} b_1 + V_{m11; n00}^{n00; m1-1} b_2 + V_{m1-1; n00}^{n00; m1-1} b_3 \\ i\hbar \frac{dc_1}{dt} &= 0 \end{aligned} \right\} \quad (24)$$

¹³ \hbar refers to Planck's constant divided by 2π .

where the coefficients for the amplitudes are matrix elements for the energy of interaction, e.g.

$$V_{n00; m10}^{m10; n00} = \iint \psi_{m10}^*(1) \psi_{n00}^*(2) V(1, 2, t) \psi_{n00}(1) \psi_{m10}(2) d\tau_1 d\tau_2.$$

We shall solve system of equations (24) by the usual method of successive approximations, taking the low energy of interaction into consideration. As in the classical approach, we also assume here that interaction begins at time $t = 0$, at which the emitting atom is at a distance of $-v\tau/2$ from the base of the perpendicular ρ . The amplitude values for this time will be

$$\begin{aligned} a_1(0) &= a; & a_2(0) &= 0; & a_3(0) &= 0; \\ b_1(0) &= 0; & b_2(0) &= 0; & b_3(0) &= 0; & c_1(0) &= c. \end{aligned}$$

For the first approximation, we obtain the following at time τ :

$$\begin{aligned} a_1 &= a; & a_2 &= 0; & a_3 &= 0; \\ b_1 &= \frac{a}{i\hbar} \int_0^\tau V_{n00; m10}^{m10; n00} dt; & b_2 &= \frac{a}{i\hbar} \int_0^\tau V_{n00; m10}^{m11; n00} dt; \\ b_3 &= \frac{a}{i\hbar} \int_0^\tau V_{n00; m10}^{m1-1; n00} dt. \end{aligned} \quad (25)$$

If we use the expression for the matrix elements of the coordinates /401 nates,

$$\begin{aligned} (n00|x|m11) &= (m11|x|n00) = \frac{1}{2} \sqrt{\frac{2}{3}} r_{nm}, \\ (n00|x|m1-1) &= (m1-1|x|n00) = -\frac{1}{2} \sqrt{\frac{2}{3}} r_{nm}, \\ (n00|y|m11) &= (n00|y|m1-1) = \frac{i}{2} \sqrt{\frac{2}{3}} r_{nm}, \\ (m11|y|n00) &= (m1-1|y|n00) = -\frac{i}{2} \sqrt{\frac{2}{3}} r_{nm}, \\ (n00|z|m10) &= (m10|z|n00) = \frac{1}{\sqrt{3}} r_{nm}. \end{aligned}$$

where r_{nm} is the matrix element for the radial part of the wave function which corresponds to the transition between states with principal quantum members n and m and substitute the matrix elements for the dipole energy of interaction, we obtain

$$b_1 = \frac{a}{i\hbar} e^2 (n00|z|m10)^2 \int_0^\tau \frac{(1 - 3 \cos^2 \gamma)}{R^3} dt$$

$$b_2 = b_2^* = -\frac{a}{i\hbar} \frac{3\sqrt{2}}{2} e^2 (n00|z|m10)^2 \int_0^\tau \frac{\cos \gamma (\cos \alpha - i \cos \beta)}{R^3} dt.$$

If we use formula (10) and integrate, then as $\tau \rightarrow \infty$ we obtain

$$b_1 = \frac{a}{i\hbar} 2e^2 (n00|z|m10)^2 \frac{1}{v^2} (1 - \cos^2 \gamma_1 - 2 \cos^2 \gamma_2),$$

$$b_2 = b_2^* = -\frac{a}{i\hbar} \sqrt{2} e^2 (n00|z|m10)^2 \frac{1}{v^2} [\cos \gamma_1 (\cos \alpha_1 - i \cos \beta_1) + 2 \cos \gamma_2 (\cos \alpha_2 - i \cos \beta_2)].$$

For the sum of the squares of the moduli of the probability amplitudes we have

$$|b_1|^2 + |b_2|^2 + |b_3|^2 = a^2 \frac{4e^4}{\hbar^2 v^2} \sin^2 \gamma_1 (n00|z|m10)^4. \quad (26)$$

The change in the amplitude of the excited state during the time /402 of passing will occur in the second approximation. If we consider the normalizing condition

$$|a_1|^2 + |b_1|^2 + |b_2|^2 + |b_3|^2 + |c_1|^2 = |a|^2 + |c|^2,$$

and the fact that the weighting of the state $\psi_{n00}(1)\psi_{n00}(2)$ does not change, we obtain the following expression for the change in the square of the amplitude of the excited state:

$$\Delta|a|^2 = |a_1|^2 - |a|^2 = -(|b_1|^2 + |b_2|^2 + |b_3|^2) =$$

$$= -|a|^2 \frac{4e^4}{\hbar^2 p^4 v^2} \sin^2 \gamma_1 (n00|z|m10)^4.$$

If, in place of the matrix element, we introduce oscillator strength, which in the formula

$$f_{nm} = \frac{2m}{\hbar} \omega_{nm} (n00|z|m10)^2 \quad (27)$$

corresponds to the $m \rightarrow n$ transition, we finally obtain

$$\Delta|a|^2 = -|a|^2 \frac{e^4}{m^2 \omega_{nm}^2} f_{nm}^2 \frac{1}{p^4 v^2} \sin^2 \gamma_1. \quad (28)$$

Let us determine the total change in probability due to the successive passes of the emitting atom close to the unexcited atoms. We can use expression (28) up to $\Delta|a|^2 = |a|^2$; this equation gives us the minimum ρ_0 up to which we can still consider pass range to be long (cf. the classical approach), i.e.

$$\rho_0 = \sqrt{\frac{e^2}{m \omega_{nm}} \cdot f_{nm} \cdot \frac{1}{v}}. \quad (29)$$

The number of atoms which appear within 1 sec and lie between ρ and $\rho + d\rho$ is equal to $2\pi\rho d\rho v N$ (N is the number of atoms in cm^2). We obtain the total change in probability during this time by integrating with respect to ρ from ρ_0 to ∞ :

$$\frac{d|a|^2}{dt} = -|a|^2 \frac{e^4}{m^2 \omega_{nm}^2} f_{nm}^2 \frac{1}{v^2} \sin^2 \gamma_1 \int_{\rho_0}^{\infty} \frac{2\pi\rho d\rho}{p^4} v N =$$

$$= -\pi^2 |a|^2 \frac{e^2}{m \omega_{nm}} f_{nm} N \sin^2 \gamma_1$$

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and, after averaging over γ_1 ,¹⁴ we obtain

$$|a|^2 = |a_0|^2 e^{-\gamma_1 t}; \quad a_0 = \frac{2\pi}{3} \frac{e^2}{m\omega_{nm}} f_{nm} N. \quad (30)$$

It can be seen from this that the excited state has a finite life which depends upon gas density.

We use Dirac's theory of light to determine radiation. If we designate the amplitude of the probability that the atom will be in state n and the field will be in the state determined by quantum numbers $N_1 N_2 \dots$ as $a_n, N_1 N_2 \dots$, the equations for determining the amplitudes will have the following form:¹⁵

$$i\hbar \frac{da_{n', N'_1 N'_2 \dots}}{dt} = \sum_{n, N_1 N_2 \dots} H_{n', N'_1 N'_2 \dots; n, N_1 N_2 \dots} a_{n, N_1 N_2 \dots} e^{i \frac{E_{n', N'_1 N'_2 \dots} - E_{n, N_1 N_2 \dots}}{\hbar} t} \quad (31)$$

where $H_{n', N'_1 N'_2 \dots; n, N_1 N_2 \dots}$ is the matrix element for the energy of interaction between the atom and the field. If we assume that the atom is excited at $t = 0$ and the energy of the field is equal to zero, i.e. that $a_{m, 00 \dots 0_s 0 \dots} = 1$ and all remaining $a_{n', N_1 N_2 \dots} = 0$, an appreciable weighting will occur with time: first of all, on the excited state in the simultaneous absence of quanta in the radiation field ($a_{m, 00 \dots 0_s 0 \dots}$); secondly, on the unexcited state, likewise without quanta in the field ($a_{n, 00 \dots 0_s 0 \dots}$); and, thirdly, on the unexcited state in the simultaneous presence of a quantum of type s ($a_{n, 00 \dots s 0 \dots}$), the frequency of which must be close to the frequency corresponding to the $m \rightarrow n$ transition. The latter will also determine the emission spectrum which is of interest to us. If we neglect the remaining

¹⁴ See Supplement I.

¹⁵ For example, see [17].

amplitudes in system of equations (31), we obtain the following equations for determining the probability amplitudes of the excited radiation field:

$$ih \frac{da_{n, \infty \dots 1, 0 \dots}(t)}{dt} = H_{m, \infty \dots 0, 0 \dots}^{n, \infty \dots 1, 0 \dots} a_{m, \infty \dots}(t) e^{-i(\omega_{nm} - \omega_s)t},$$

where ω_{nm} is the frequency of the $m \rightarrow n$ transition, and ω_s is radiation frequency. If we substitute the expression found above and the expression from formula (30) for the probability amplitude of the excited state of the atom as a function of time¹⁶, i.e.

$$a_{m, \infty \dots}(t) = a(t) = e^{-\frac{\nu_0}{2}t}$$

into the right member, we obtain the following for the amplitudes being sought:

$$a_{n, \infty \dots 1, 0 \dots}(t) = H_{m, \infty \dots 0, 0 \dots}^{n, \infty \dots 1, 0 \dots} \frac{e^{i(\omega_s - \omega_{nm})t - \frac{\nu_0}{2}t} - 1}{-i \left[\omega_s - \omega_{nm} + i \left(\frac{\nu_0}{2} \right) \right]}. \quad (32)$$

As $t \rightarrow \infty$, the atom goes to the ground state and a certain probability for excitation of the field occurs; the probability distribution for energy in the radiation field at this time, by frequency, will be:

$$I(\omega) = \text{const} |a_{n, \infty \dots 1, 0 \dots}(\infty)|^2 = \frac{\text{const}}{(\omega - \omega_{nm})^2 + \left(\frac{\nu_0}{2} \right)^2}. \quad (33)$$

¹⁶ It can easily be seen from equation (24) that the phase of the excited state is independent of time in the approximations considered.

which agrees with the emission spectrum of the decaying classical oscillator, for which $\omega_0 = \omega_{nm}$. For line width, we obtain the expression

$$\delta_r = \frac{H_0}{2} = \frac{\pi}{3} \frac{e^2}{m\omega_{nm}} f_{nm} N \quad (34)$$

which differs from formula (19), derived from classical considerations, only by a factor of f_{nm} . /405

We had assumed here that the line considered corresponds to the atom's transition to the ground state, but we can easily see that it need not necessarily be so. The effect mentioned will also have an influence on the width of those lines which correspond to the transition between two higher levels if a transition to the ground state is not forbidden, at least for one of them.

5. Concluding Remarks

The ideas developed, based on a consideration of radiation from one atom, are applicable only to gas densities which are not very great. At higher density, when the "free path time" of the atom becomes comparable to "collision time," a radiation also becomes appreciable in the spectrum that occurs within the time of principal interaction between the atoms. This radiation may no longer be viewed as if it propagated from one atom; rather, we must study the radiation from the diatomic system which forms, as a whole. It does not appear possible to us to take the effect of the radiation on the form and width of the spectral line during collision time into consideration exactly, so we limit ourselves to a qualitative study of this effect. Strictly speaking, we would have to know the exact form of the function that describes the light wave in order to find the emission spectrum, and we would then have to resolve it into a Fourier

integral. Since this is impossible, we must be satisfied -- as is usually done in such cases -- with the qualitative determination of frequencies that are emitted during collisions. If we assume that the intensity of these frequencies in the spectrum is proportional to their lives, we can draw a number of conclusions regarding the form and width of the line even at relatively high density¹⁷.

Thus at relatively high density, the emitting atom will often /406 be close to another atom of the same type; in order to study the radiation which occurs here, we can consider these two atoms as a molecule in which the levels which result upon the dissociation of an excited and an unexcited atom are excited. The wave function for such a molecule can, in the 0th approximation, be formulated in the form of a linear combination of products of the functions for the isolated atoms. We calculate the frequency of the light which is emitted by such a molecule, taking the dipole energy of interaction between the atoms generating it into consideration as a perturbation. We can neglect the degeneracy of the system due to electron exchange and take only energy exchange into consideration; this is immediately permissible in the problem under discussion. If we orient one of the coordinate axes, e.g. ζ , along a line connecting the atoms, we obtain the following form for the formula for the dipole energy of interaction (6):

$$V = \frac{e^2}{R^3} (\xi_1 \xi_2 + \eta_1 \eta_2 - 2\zeta_1 \zeta_2). \quad (35)$$

The excited molecule can be in a Σ or a Π state, the latter being doubly degenerate corresponding to the two directions of rotation. The eigenfunctions for these states -- they will be

¹⁷ For example, see [4].

prominent precisely because of perturbation (35) -- can be formulated as follows in the 0th approximation:

$$\left. \begin{aligned} \Psi_z &= \frac{1}{\sqrt{2}} \{ \psi_{n00}(1) \psi_{m10}(2) + \psi_{m10}(1) \psi_{n00}(2) \} \\ \Psi_n^+ &= \frac{1}{\sqrt{2}} \{ \psi_{n00}(1) \psi_{m11}(2) + \psi_{m11}(1) \psi_{n00}(2) \} \\ \Psi_n^- &= \frac{1}{\sqrt{2}} \{ \psi_{n20}(1) \psi_{m1-1}(2) + \psi_{m1-1}(1) \psi_{n00}(2) \} \end{aligned} \right\} \quad (36)$$

Here, $\psi_{n00}(1)$, $\psi_{m10}(2)$, etc., represent the eigenfunctions for the first and second atoms, respectively, in each case. The subscripts refer to the values of quantum numbers n , l and m of the particular state¹⁸. Accordingly, the change in energy due to /407 perturbation (35) will be

$$\begin{aligned} \varepsilon_z &= \int \Psi_z^* V \Psi_z d\tau = -\frac{e^2}{m\omega_0} f \frac{1}{R^3} h, \\ \varepsilon_n &= \int \Psi_n^* V \Psi_n d\tau = +\frac{1}{2} \frac{e^2}{m\omega_0} f \frac{1}{R^3} h. \end{aligned}$$

Here, f is oscillator strength, which is determined by relation (27). From this we obtain the emitted frequencies

¹⁸ The system being considered, consisting of two identical atoms in a state at lowest energy, is not degenerate and is described in the 0th approximation by the function $\psi_{n00}(1)\psi_{m10}(2)$; the next, first excited state, the only one in which we are interested, on the other hand, already possesses six-fold degeneracy; if we calculate by the conventional method of perturbation theory, with interaction energy (35), we find that this degeneracy is partly eliminated, and symmetrical expressions (36) are functions in the 0th approximation, as are the antisymmetric expressions, although we did not take the latter into consideration, since the states corresponding to them do not combine with the ground state and therefore did not manifest themselves in radiation.

$$\begin{aligned}\omega' &= \omega_0 + \varepsilon_2 h = \omega_0 - \frac{e^2}{m\omega_0} f \frac{1}{R^3} \\ \omega'' &= \omega_0 + \varepsilon_1 h = \omega_0 + \frac{1}{2} \frac{e^2}{m\omega_0} f \frac{1}{R^3}\end{aligned}\quad (37)$$

We can interpret these calculations classically as follows: If we assume that the two similar three-dimensional oscillators are separated by a distance R which is small compared to the length of the light wave and that they interact with the aid of the dipole fields in accordance with (35), then the oscillations of the oscillators along similar coordinate axes will be linearly coupled in pairs; oscillation ξ_1 will be coupled only with ξ_2 , ξ_1 with ξ_2 , and η_1 with η_2 . Each pair will possess two normal frequencies which correspond to the parallel and antiparallel oscillations. Only the parallel oscillations will be optically active, while the antiparallel oscillations will not be operant in emission, since no change in electrical moment is associated with them. The frequency emitted as the result of oscillation on ξ will be shifted toward the red, but those on ξ and η , toward the violet; the magnitudes of the shift will also be equal in the first approximation here, up to the factor f , which figures in expressions (37).

Thus the radiation during interaction will result in a certain additional asymmetric broadening. To be sure, the asymmetry will not be gross, for although the frequency shift in the red direction is twice as large as that in the violet direction, the statistical weighting on this shift is itself only half as great. It seems to us that it would be impossible to say anything more precise concerning the form and width of the line. It must be noted here, however, that this peculiar "Zeemann effect" (in the sense that the degeneracy with respect to m is partly eliminated in its case) has no little influence, due to the relatively slow decreases in interaction forces with distance. We must therefore consider our expression (21) to be a lower limit on the broadness

of the spectral line in a homogeneous gas; this should agree with experiment in all cases.

We note in closing that transferred energy ϵ in our formula (13) is a function of the angle which the direction of the relative motion of the atoms forms with the direction of oscillation; we should also be able to find this asymmetry of cross section experimentally, e.g. with a molecular beam. We hope to be able to discuss this problem in greater detail elsewhere, as well as the effect of the interaction of similar atoms on the polarization of resonance fluorescence and selective scattering.

SUPPLEMENT I

Calculation of Total Energy Loss Resulting From a Large Number of Passes

When the emitting atom passes close to an unexcited atom, the energy lost is

$$\epsilon = E \frac{e^4}{m^2 \omega_0^4} \frac{1}{r^2 \rho^4} \sin^2 \gamma_1. \quad (13)$$

In order to determine the total change in energy which is caused by successive passes, we imagine, for the sake of simplicity, that all atoms, including the emitting one, move at velocities which are equal in absolute value and randomly oriented or -- what amounts to the same thing -- that the emitting atom is immobile, and the remaining atoms move all around the emitting atom; a negative velocity for the emitting atom itself must be added to their random velocities. The various passes will differ in range ρ and the angle γ_1 between the direction of the emitting atom's electrical moment and the velocity \mathbf{v} of relative motion. The presence of motion on the part of the nonemitting atoms, too, is important for the problem being treated, since it determines averaging over γ_1 . It is interesting that motion only on the part

of the emitting atom in an environment of immobile atoms does not yield the required line width when only long pass ranges are considered. The reason for this is that the intensity of radiation is determined in this case primarily by the emitting atoms with electrical moments oriented along the lines of passage ($\gamma_1 = 0$), for which, however, decay is equivalent to natural decay.

If the z-axis is oriented opposite to the absolute velocity of the emitting atom, we obtain:

$$v = 2u \cos \theta$$

for the magnitude of the relative velocity of the other atom, where θ indicates the angle between relative velocity v and the z-axis. The angles θ and ϕ of relative velocity v are connected to the angles θ and ϕ of the absolute velocity of the unexcited atom by the relations

$$\theta = \theta/2, \quad \phi = \phi.$$

If we use α to designate the angle between the direction of the electrical moment p of the emitting atom and the z-axis, we obtain the expression

$$\cos \gamma_1 = \cos \alpha \cos \theta + \sin \alpha \sin \theta \cos \phi \quad (38)$$

for the angle γ_1 from the spherical triangle formed by (z, v, p) . The probability that the absolute velocity of the unexcited atom is in a direction between θ and $\theta + d\theta$, ϕ and $\phi + d\phi$ will be

$$W(\theta, \phi) d\theta d\phi = \frac{\sin \theta d\theta d\phi}{4\pi}.$$

For relative velocity we then have, correspondingly,

$$W(\theta, \phi) d\theta d\phi = \frac{\sin 2\theta d\theta d\phi}{2\pi}.$$

Since energy will essentially be transferred when the passing atom is located close to the base of the perpendicular ρ , we shall assume that all those atoms receive energy that cross the plane which is perpendicular to their paths and contains the emitting atom. The number of atoms which pass at a distance between ρ and $\rho + d\rho$ from the emitting atom in the directions θ and ϕ during time element dt is

$$dn = N W(\theta, \phi) d\theta d\phi 2\pi \rho d\rho dt = N v dt \rho d\rho \sin 2\theta d\theta d\phi. \quad (39)$$

For the total quantity of energy which is lost to the group of atoms dn , we thus obtain the following from formulas (13), (38) and (39):

$$dn = E \frac{e^4}{m^2 \omega_0^2} N dt \frac{d\rho}{\rho^3} \frac{1}{v} \sin 2\theta d\theta d\phi \{1 - (\cos \alpha \cos \theta + \sin \alpha \sin \theta \cos \phi)\}^2.$$

We obtain the total energy loss for time dt by integrating with respect to the three variables: from ρ_0 to ∞ with respect to ρ ; from 0 to $\pi/2$ with respect to θ ; and from 0 to 2π with respect to ϕ .

Integration with respect to ρ and ϕ yields

$$dE = -E \frac{e^4}{m^2 \omega_0^2} N \frac{\pi}{\rho_0^3 v} \sin 2\theta d\theta \left\{1 - \cos^2 \alpha \cos^2 \theta - \frac{1}{2} \sin^2 \alpha \sin^2 \theta\right\} dt.$$

If we use formula (15) for the lower limit of ρ_0 and integrate with respect to θ , we obtain

and, from this,

$$dE = -E \frac{\pi}{2} \frac{e^2}{m \omega_0} N \left(1 + \frac{1}{2} \sin^2 \alpha\right) dt,$$

where

$$E = E_0 e^{-\mu t},$$

$$\mu = \frac{\pi}{2} \frac{e^2}{m \omega_0} N \left(1 + \frac{1}{2} \sin^2 \alpha\right). \quad (40)$$

Formulas (17) and (18), in which we had neglected the slight dependence upon α , follow from the above.

Quite analogous considerations also result in formulas (30).

SUPPLEMENT II.

Determination of the Form and Width of a Line While Taking Long Pass Ranges and Close Collisions into Consideration

According to our ideas pertaining to collision, i.e. for a pass during which the distance between atoms is less than the ρ_0 determined by the formula

$$\rho_0 = \sqrt{f \frac{e^2}{m \omega_0} \frac{1}{v}} \quad (29)$$

the amplitude of the oscillator changes discontinuously and sometimes has positive, sometimes negative values after collision, the magnitudes of which do not exceed absolute value prior to collision. We therefore assume that the oscillator was not oscillating from $t = -\infty$ to $t = 0$, that it was excited at time $t = 0$, and that it was then subjected to collisions at times $t_1, t_2, \dots, t_k, \dots$, so we can write /411

$$z(t) = A_k e^{-\frac{\gamma_k}{2} t} \cos(\omega_0 t + \varphi) \quad , \quad t_k \leq t < t_{k+1} \quad (41)$$

The function $z(t)$ determined in this manner can be represented in the form of the Fourier integral

where

$$\begin{aligned} z(t) &= \int_{-\infty}^{+\infty} g(\omega) e^{i\omega t} d\omega \\ g(\omega) &= \frac{1}{2\pi} \int_0^{\infty} z(t) e^{-i\omega t} dt. \end{aligned} \quad (42)$$

In order to obtain the sought intensity distribution in the spectrum, $J(\omega)$, we must square $g(\omega)$ and take the average, i.e.

$$J(\omega) = \text{const } \overline{|g(\omega)|^2}.$$

From formulas (41) and (42), we have

$$\begin{aligned} g(\omega) &= \frac{1}{4\pi} \sum_{k=0}^{\infty} A_k \int_{t_k}^{t_{k+1}} \left[e^{i[(\omega_0 - \omega)t + \tau] - \frac{\mu_0}{2}t} + e^{-i[(\omega_0 + \omega)t + \tau] - \frac{\mu_0}{2}t} \right] dt = \\ &= \frac{1}{4\pi} \sum_{k=0}^{\infty} A_k \left\{ \frac{e^{i[(\omega_0 - \omega)t_{k+1} + \tau] - \frac{\mu_0}{2}t_{k+1}} - e^{i[(\omega_0 - \omega)t_k + \tau] - \frac{\mu_0}{2}t_k}}{i(\omega_0 - \omega) - \mu_0/2} - \right. \\ &\quad \left. - \frac{e^{-i[(\omega_0 + \omega)t_{k+1} + \tau] - \frac{\mu_0}{2}t_{k+1}} - e^{-i[(\omega_0 + \omega)t_k + \tau] - \frac{\mu_0}{2}t_k}}{i(\omega_0 + \omega) + \mu_0/2} \right\}. \end{aligned} \quad (43)$$

In the vicinity of the line, i.e. for the values of ω_0 close to ω , we can neglect the second term in this formula; when we then find $|g(\omega)|^2$ and average it, we see that the terms with the product $A_k A_{k'}$ vanish for $k \neq k'$, due to the assumption made regarding the behavior of amplitudes upon collision, so we can immediately omit them and write

$$\begin{aligned} |g(\omega)|^2 &= \frac{1}{16\pi^2} \sum_{k=0}^{\infty} A_k^2 e^{-\mu_0 t_k} \left| \frac{e^{i(\omega_0 - \omega)\tau_k - \frac{\mu_0}{2}\tau_k} - 1}{i(\omega_0 - \omega) - \frac{\mu_0}{2}} \right|^2 = \\ &= \frac{1}{16\pi^2} \sum_{k=0}^{\infty} A_k^2 e^{-\mu_0 t_k} \left\{ \frac{1 + e^{-\mu_0 \tau_k} - 2e^{-\frac{\mu_0}{2}\tau_k} \cos(\omega_0 - \omega)\tau_k}{(\omega_0 - \omega)^2 + \left(\frac{\mu_0}{2}\right)^2} \right\} \end{aligned} \quad (44)$$

where

$$\tau_k = t_{k+1} - t_k$$

refers to the time between two successive collisions. The quantities A_k , t_k and τ_k are independent of one another; we can

therefore average separately for them; averaging yields a certain /412 constant for the first two quantities which is independent of ω and thus is of no importance for intensity distribution in the spectrum. In order to average over τ_k , we proceed by the usual method. The probability that τ_k lies between τ and $\tau + d\tau$ is

$$dw = \frac{1}{\tau_0} e^{-\frac{\tau}{\tau_0}} d\tau.$$

Here, τ_0 is the mean time between two collisions, given by

$$\tau_0 = \frac{1}{\pi \rho_0^2 N v} \quad (45)$$

Thus we obtain

$$J(\omega) = \text{const} \cdot \overline{|g(\omega)|^2} = \text{const} \cdot \int_0^\infty \frac{1 + e^{-\frac{\tau}{\tau_0}} - 2e^{-\frac{\mu_0}{2}\tau} \cos(\omega_0 - \omega)\tau}{(\omega_0 - \omega)^2 + \left(\frac{\mu_0}{2}\right)^2} \cdot e^{-\frac{\tau}{\tau_0}} d\tau.$$

The integrals which occur here can be taken from tables. When we evaluate them and make elementary transformations, we finally obtain

$$J(\omega) = \frac{\text{const}}{(\omega_0 - \omega)^2 + \left(\frac{1}{\tau_0} + \frac{\mu_0}{2}\right)^2}, \quad (46)$$

i.e. the dispersion distribution with width

$$\delta = \frac{1}{\tau_0} + \frac{\mu_0}{2}.$$

Taking (45), (29) and (30) into consideration, we obtain (21) for the width of the spectral line in a homogeneous gas.

Strictly speaking, we would have to use μ , which is given by relation (40) (up to a factor of f) in place of μ_0 everywhere, and later we would have to average with α (46). However, this

results in a formula which is not immediately clear and which yields a curve for the quantity $J(\omega)$ that deviates somewhat from the dispersion curve only close to the center of the line and could hardly have physical meaning. We can thus neglect the small term which is a function of α or use its mean directly, as has been done here.

In closing, we consider it to be our pleasant duty to express our most cordial thanks to Profs. I. Y. Tamm and M. A. Leontovich for their attention to and interest in this work.

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